

What is claimed is:

1. A process for selectively adsorbing a component of a gas mixture, which comprises contacting the mixture with a solid state, selective adsorbent material comprising a porous framework of a plurality of transition element complexes (TECs) having the formula shown in Figure 1, wherein:

(a) M is a primary transition metal ion;
(b) D to D₄ are primary donors and m is zero or one, at least three of D to D₄ occupying primary donor coordination sites on M but leaving at least one open coordination site on M for the component to react with M;

(c) G to G₄ are functional groups and n is zero or one, at least one of G to G₄ being intramolecularly bonded to at least three adjacent primary donors to form at least one 5 or 6 member chelate ring on the primary transition metal ion and providing at least three donors thereto;

(d) M, D to D₄ and G to G₄ together define one or more transition metal complexes, wherein said complexes are the same or different and wherein k is from 0 to 4;

(e) R is an intermolecular connecting group selected from

(i) secondary metal ions coordinated with secondary donors bonded to one or more of groups G to G₄ on the respective TECs;

(ii) multifunctional organic groups forming covalent bonds with one or more of groups G to G₄ on the respective TECs;

(iii) functional groups forming hydrogen bonds with one or more of groups G to G₄ on the respective TECs; or

(iv) non-coordinating counter-ions spaced between and separating the respective TECs; the R group bonding and/or spacing the respective TECs to and from one another to maintain them in a porous framework wherein z is from 1 to 8, and wherein R may be the same or different when z is greater than 1; and (f) y is an integer sufficient to provide said porous framework of the plurality of TECs for the selective adsorption of the desired component thereon.

2. The process of claim 1 for selectively adsorbing a component of a gas mixture, wherein said transition metal ion M is an element selected from the first, second or third row of transition metals of the Periodic Table and the lanthanides.

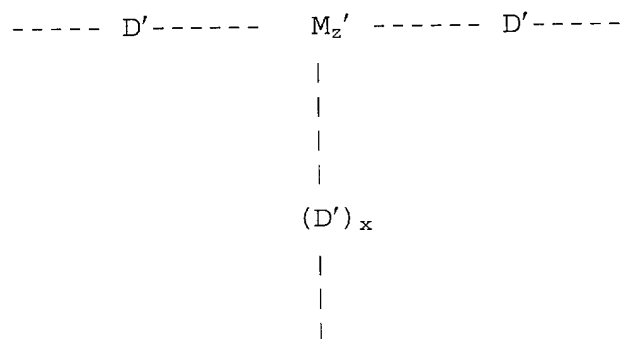
3. The process of claim 1 for selectively adsorbing a component of a gas mixture, wherein the donors D to D₄ are N, O, S, C, P, Cl, F, or Br, and may be neutral or charged.

4. The process of claim 1 for selectively adsorbing a component of a gas mixture, wherein G to G₄ may be the same or different and are:

- a) pyridinyl or imidazolyl groups;
- b) amino groups having the formula $-NR^1R^2R^3$;
- c) imino groups having the formula $-R^1N=CR^2R^3$ or $-N=CR^1R^2$;

- d) carbonyl groups having the formula - $R^1C(O)R^2$, $-R^1CONR^2R^3$ or $-R^1CO_2R^2$;
 - e) cyano groups having the formula $-R^1-CN$;
 - f) nitro groups having the formula $-R^1-NO_2$;
 - g) phenolate groups with up to five substituents selected from halogens or $-R^1$;
 - h) carboxylate groups having the formula $-R^1CO_2-$; and
 - i) alkoxy groups having the formula $-R^1O^-$;
- wherein R^1 , R^2 and R^3 are the same or different and are substituted or unsubstituted acyclic or carbocyclic groups, or substituted by F, Cl, Br, O, N, P, S, Si or B.

5. The process of claim 1 for selectively adsorbing a component of a gas mixture, wherein R is a member of group (i) and has the structure



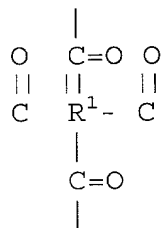
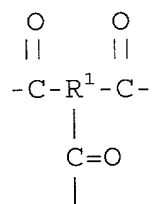
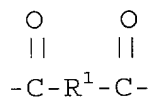
wherein D' is a secondary donor or a group of 2 to 4 secondary donors bonded to at least a G to G_4 group or a chelate ring on a coordination site on M and may also bond to an adjacent R group within the porous framework; and M' is a secondary metal ion coordinated

with secondary donors D', x is from 0 to 6 and z is from 1 to 8; said structure bonding the respective TECs to one another to form said porous framework.

6. The process of claim 5 for selectively adsorbing a component of a gas mixture, wherein the TECs are $\text{Co}(\text{Me}_2\text{Ac}_2\text{H}_2\text{malen})(4\text{-Py-O}^-)$.

7. The process of claim 5 for selectively adsorbing a component of a gas mixture, wherein the TECs are $\text{Co}(\text{Me}_2\text{Ac}_2\text{H}_2\text{maltmen})(4\text{-Py-O}^-)$.

8. The process of claim 1 for selectively adsorbing a component of a gas mixture, wherein R is a member of group (ii) and has the formula



or mixtures thereof, and wherein R^1 is a substituted or unsubstituted acyclic or carbocyclic group and is unsubstituted or is substituted by F, Cl, Br, O, N, P, S, Si or B.

9. The process of claim 8 for selectively adsorbing a component of a gas mixture, wherein the TEC is $\text{Co}(\text{Me}_2\text{H}_2\text{H}_2\text{malophen})\text{Py}$.

10. The process of claim 1 for selectively adsorbing a component of a gas mixture, wherein R is group (iii) and is:

- a) an amide group having the formula $R^1\text{CONR}^2-$;
- b) an amino group having the formula $R^1R^2\text{N}-$;
- c) a carbinol group having the formula $-\text{R}^1\text{OH}$; or
- d) a carboxylic acid group having the formula $-\text{R}^1\text{CO}_2\text{H}$,

wherein R^1 and R^2 are the same or different and are unsubstituted acyclic or carbocyclic groups, or substituted acyclic or carbocyclic groups substituted by F, Cl, Br, O, N, P, S, Si or B.

11. The process of claim 1 for selectively adsorbing a component of a gas mixture, wherein R is a member of group (iv), selected from:

- (a) an alkylammonium or arylammonium cation having the formula $-(R^1R^2R^3R^4)\text{N}^+$, wherein $R^1R^2R^3$ and R^4 are the same or different and are hydrogen and at least one of which is an unsubstituted acyclic or carbocyclic group or an acyclic or carbocyclic group substituted

by F, Cl, Br, O, N, P, S, Si or B when the TECs are anionic; or

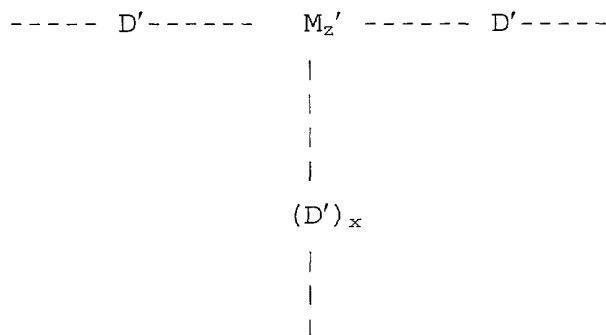
- (b) BF_4^- , BOR''^- , PF_6^- , NO_3^- , SO_4^{2-} , CO_3^{2-} , MoO_4^{2-} , a polyoxometallate, $\text{R}''\text{CO}_2^-$, $\text{R}''\text{O}^-$, $\text{R}''\text{SO}_3^-$, wherein R'' is a C_{1-20} alkyl or an aryl or hetero group having from 4 to 20 carbon atoms, when the TECs are cationic.

12. A process for selectively adsorbing oxygen from a gas mixture, which comprises contacting the mixture with a solid state, selective adsorbent material comprising a porous framework of a plurality of transition element complexes (TECs) having the formula shown in Figure 3, wherein:

- (a) M is a primary transition metal ion selected from Co(II) , Fe(II) or Mn(II) ;
- (b) D to D_4 are primary donors occupying primary donor coordination sites on M but leaving one open coordination site on M for an oxygen molecule to react with M;
- (c) G to G_4 are functional groups and n is zero or one, at least one of G to G_4 being intramolecularly bonded to at least three adjacent primary donors to form at least one 5 or 6 member chelate ring on the primary transition metal ion and providing at least three donors thereto;
- (d) M, D to D_4 and G to G_4 together define one or more transition metal complexes TEC A, TEC B and TEC C, wherein said complexes are the same or different;

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- (e) D' is a secondary donor or a group of secondary donors bonded to a chelate ring on a coordination site on M, and x is zero or one;
- (f) M' is a secondary metal ion coordinated with secondary donors D',



the group bonding the respective TECs to one another to maintain them in a porous framework and wherein z is from 1 to 8 and x is from 0 to 6; and

- (g) y is an integer sufficient to provide said porous framework of the plurality of TECs for the selective adsorption of oxygen thereon.

13. A composition for selectively adsorbing a component of a gas mixture, which comprises a solid state, selective adsorbent material comprising a porous framework of a plurality of transition element complexes (TECs) having the formula shown in Figure 1, wherein:

- (a) M is a primary transition metal ion;

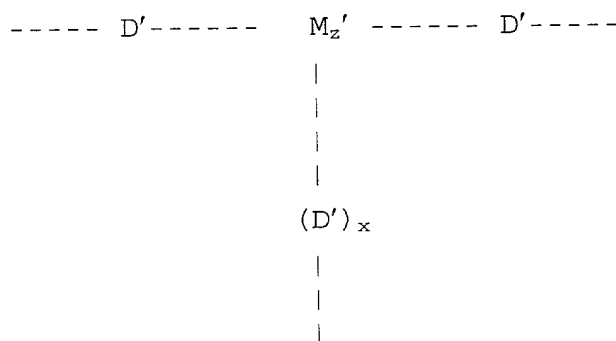
- (b) D to D₄ are primary donors and m is zero or one, at least three of D to D₄ occupying primary donor coordination sites on M but leaving at least one open coordination site on M for the component to react with M;
- (c) G to G₄ are functional groups and n is zero or one, at least one of G to G₄ being intramolecularly bonded to at least three adjacent primary donors to form at least one 5 or 6 member chelate ring on the primary transition metal ion and providing at least three donors thereto;
- (d) M, D to D₄ and G to G₄ together define one or more transition metal complexes, wherein said complexes are the same or different and k is from 0 to 4;
- (e) R is an intermolecular connecting group selected from
 - (i) secondary metal ions coordinated with secondary donors bonded to one or more of groups G to G₄ on the respective TECs;
 - (ii) multifunctional organic groups forming covalent bonds with one or more of groups G to G₄ on the respective TECs;
 - (iii) functional groups forming hydrogen bonds with one or more of groups G to G₄ on the respective TECs; or
 - (iv) non-coordinating counter-ions spaced between and separating the respective TECs;

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the R group bonding and/or spacing the respective TECs to and from one another to maintain them in a porous framework, wherein z is from 1 to 8, and wherein R may be the same or different when z is greater than 1; and

- (f) y is an integer sufficient to provide said porous framework of the plurality of TECs for the selective adsorption of the desired component thereon.

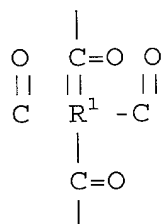
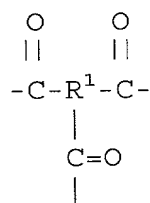
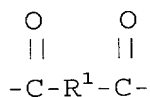
14. The composition of claim 13 for selectively adsorbing a component of a gas mixture, wherein R is a member of group (i) and has the structure



wherein D' is a secondary donor or a group of two to four secondary donors bonded to a chelate ring on a coordination site on M but may also bond to an adjacent R group within the porous framework; and M' is a secondary metal ion coordinated with secondary donors D', wherein z is from 1 to 8 and x is from 0 to 6; said structure bonding the respective TECs to one another to form said porous framework.

15 The composition of claim 14 for selectively adsorbing a component of a gas mixture, wherein the TECs are $\text{Co}(\text{Me}_2\text{Ac}_2\text{H}_2\text{malen})(4\text{-Py-O}^-)$ or $\text{Co}(\text{Me}_2\text{Ac}_2\text{H}_2\text{maltmen})(4\text{-Py-O}^-)$.

16. The composition of claim 13 for selectively adsorbing a component of a gas mixture, wherein R is a member of group (ii) and has the formula



or mixtures thereof, wherein R^1 is a substituted or unsubstituted acyclic or carbocyclic group and is unsubstituted or is substituted by F, Cl, Br, O, N, P, S, Si or B.

17. The composition of claim 16 for selectively adsorbing a component of a gas mixture, wherein the TECs are $\text{Co}(\text{Me}_2\text{H}_2\text{H}_2\text{malophen})\text{Py}$.

18. The composition of claim 16 for selectively adsorbing a component of a gas mixture, wherein the TECs are $\text{Co}(\text{Me}_2\text{H}_2\text{H}_2\text{maltmen})(4\text{-PyOLi})$.

19. The composition of claim 16 for selectively adsorbing a component of a gas mixture, wherein the TECs are $\text{Co}(\text{Me}_2\text{H}_2\text{H}_2\text{maldmen})(4\text{-PyOLi})$.

20. The composition of claim 13 for selectively adsorbing a component of a gas mixture, wherein R is a member of group (iii) and is:

- a) an amide group having the formula R^1CONR^2- ;
- b) an amino group having the formula $\text{R}^1\text{R}^2\text{N}-$;
- c) a carbinol group having the formula $-\text{R}^1\text{OH}$; or
- d) a carboxylic acid group having the formula $-\text{R}^1\text{CO}_2\text{H}$,

wherein R^1 and R^2 are the same or different and are unsubstituted acyclic or carbocyclic groups, or substituted acyclic or carbocyclic groups substituted by F, Cl, Br, O, N, P, S, Si or B.

21. The composition of claim 12 for selectively adsorbing a component of a gas mixture, wherein R is a member of group (iv), selected from:

- (a) an alkylammonium or arylammonium cation having having the formula $-(\text{R}^1\text{R}^2\text{R}^3\text{R}^4)\text{N}^+$, wherein R^1 , R^2 , R^3 and R^4 are the same or different and are hydrogen and at least one of which is an unsubstituted acyclic or carbocyclic group or an acyclic or carbocyclic group substituted by F, Cl, Br,

O, N, P, S, Si or B when the TECs are anionic; or

- (b) BF_4^- , BOR''^- , PF_6^- , NO_3^- , SO_4^{2-} , CO_3^{2-} , MoO_4^{2-} , a polyoxometallate, $\text{R}''\text{CO}_2^-$, $\text{R}''\text{O}^-$, $\text{R}''\text{SO}_3^-$, wherein R'' is a C_{1-20} alkyl or an aryl or hetero group having from 4 to 20 carbon atoms, when the TECs are cationic.